

SURFACE-CATALYZED RECOMBINATION INTO EXCITED ELECTRONIC,
VIBRATIONAL, ROTATIONAL, AND KINETIC ENERGY STATES: A REVIEW

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Abstract. Laboratory experiments in which recombined CO, CO₂, D₂O, OH, N₂, H₂, and O₂ molecules desorb from surfaces in excited internal and translational states are briefly reviewed. Unequilibrated distributions predominate from the principally catalytic-metal substrates so far investigated. Mean kinetic energies have been observed up to ~3x, and in some cases less than, wall-thermal; the velocity distributions generally vary with emission angle, with non-Lambertian particle fluxes. The excitation state populations are found to depend on surface impurities, in an as yet unexplained way.

Introduction

Several small-molecular species have been found to desorb after formation on laboratory surfaces with internal and kinetic energy distributions (and angular fluxes) markedly different from those that would result from their equilibration at the substrate's temperature. The observations for neutral molecules other than NO₂ and NO, which are reviewed separately in the accompanying paper by Barrett and Kofsky [these Proceedings] (with further data on NO* in Kofsky and Barrett [these Proceedings]), are listed in Table 1.

Discussion

This lack of equilibration, and a comparably common non-Boltzmann (statistical) distribution of desorption quantum states, are an at least qualitatively expected outcome of the dynamics of the surface reaction complex from which the molecular fragment originates [Polanyi, 1972; Tully, 1980; Kori and Halpern, 1983; Ceyer et al., 1983]. Indeed, our literature survey identified only one measurement of complete rotational and vibrational thermalization of a recombination product, OH on polycrystalline Pt [Talley et al., 1981] (item [14] in Table 1), curiously that very species initially considered responsible for spacecraft glow [by several groups]. This result was interpreted [Talley et al., 1981] as due to the rate of desorption of hydroxyl excited in Langmuir-Hinshelwood (among species present on the surface) reactions of O with H being small compared with the rate of collisional equilibration of the adsorbed radical with its substrate. We briefly touch on the more sophisticated theoretical arguments after reviewing the database of Table 1.

These quantum state-specific measurements were made using passive spectrometry, tuned laser and (to a lesser extent) electron beam induced fluorescence, and for the velocity distributions, time-of-flight and most recently laser Doppler methods [Cavanagh and King, 1984]. (Some qualitative reports of experiment results that were later verified have been omitted, as have gas-phase reactions of precursors formed on sur-

faces.) About half were performed in ultrahigh vacuum systems in which the surface crystal structure and its contamination (at the sub-monolayer level) could be characterized in situ by low-energy electron diffraction, Auger electron spectroscopy, and similar surface-science technologies. In the experiments indicated one reactant (or an impurity) was initially incorporated into the target surface, and in some others the atomic species was made to permeate through the sample from its back side; this of course does not mean that reactants from the beam also do not become adsorbed on, and in some experiments dissociated on, the substrate. (Molecules such as N_2 and NO have zero activation energy for dissociation on some transition metal crystal planes.) All but one set of the measurements (those of Harteck's group, [3], [11], [12], and [13] in Table 1) have been done within the last 6 years. The discipline and diagnostics have not yet developed to a stage at which all the internal quantum states of a desorbate as functions of its translational energy and angle of emission have been measured simultaneously.

The list refers to heterogeneous recombination involving species incident (or diffusing) at mean velocities <1 km/sec and thus kinetic energies $<1/2$ eV. Some of these combine (as mentioned) with surface dopants, in processes that might be referred to as selective chemical sputtering into molecular states, or alternatively as reactive scattering. It does not include non-associative molecule scattering [Asscher et al., 1985] or desorption [Cavanagh and King, 1984] experiments, many of which also provide evidence for nonequilibration and non-Lambertian ($\cos^1 \{\text{angle } \theta \text{ to the normal}\}$) effluent flux distributions. In addition it specifically omits physical sputtering, which refers to neutral or ionized incident particles with directed kinetic energy greater than the few tens eV threshold for dislodging atoms and complexes from the surface, some of which are ionized or in electronically excited states (reviewed in the context of spacecraft glows by Kofsky [1984]).

In this regard, most of the existing information about the ablative reactions with surface materials of 8 km/sec relative velocity atoms and molecules, such as those at orbital altitudes, comes from shuttle and other spacecraft exposure experiments/tests rather than the laboratory or theory. While the incident 5-eV oxygen atoms are well known to be associated with the mass loss and texturing of various types of exposed surfaces [Visentine et al., 1985], no connection between the rates of erosion and glow emission has been identified. Further, the role played by this kinetic energy in exciting spacecraft radiations is by no means established--the signal/noise of the measurements is insufficient to rule out the possibility that the glow off forward surfaces is due merely to the ram enhancement of densities of incident atoms and molecules. The mechanism might also involve O atom-associated (and perhaps off-surface induced plasma-associated) roughening of the surface to increase its concentration of sites where physisorption, chemisorption, and excitative-desorption can take place, and/or avoidance of "catalyst poisoning"--buildup of reaction-inhibiting species on the lattice--by impact of the moderately energetic neutral (and charged) particles. In that sense, and in cases that the incident particles accommodate on the surface to participate in Langmuir-Hinshelwood reactions, the low reactant energy database of Table 1 is relevant to the spacecraft glows issue.

Most of the recombination experiments in Table 1 were done on at least partially characterized surfaces of "catalytic" transition metals, in large part toward understanding the role of these (essentially, reducing)

substrates, rather than on materials of the type exposed on orbiting spacecraft--generally, insulators. On this limited subset, recombination with nonequilibrium and nonstatistical electronic, vibrational, and kinetic energy distributions (themselves desorption-angle dependent) of the product molecule is the rule rather than the exception. Translationally cold as well as hot desorbate beams have been seen, as well as rotationally cold streams from non-associative desorption [Cavanagh and King, 1981]. Although forward focusing from the macroscopically smooth laboratory surfaces (due to the parallel orientation of the surface barrier equipotentials) is common, flux distributions flatter than $\cos^2\theta$ can also occur [Cavanagh and King, 1984]. The angular distribution of the radiating species (and potentially, the not-yet measured polarization of rotational-band emission from the desorbate) is a further diagnostic of the surface interaction that could be applicable in investigations of spacecraft glows.

Note that while CO and O have been found to recombine on room temperature glass [Pravilov and Smirnova, 1981], the comparably exoergic NO + O surface reaction was not reported in connection with the several measurements of its gas-phase rate coefficient (references [6a-e] in Barrett and Kofsky [these Proceedings]).

Surface contamination by the Group V and Group VI elements S, O, and N--readily quantifiable by Auger electron or x-ray photoelectron spectroscopy--plays a part in several of the internal excitations of the desorbed molecules; no theoretical explanation of this effect, which presumably involves formation of an intermediate complex, appears to have been advanced. Similarly, interference with the recombination-desorption process by other molecules introduced into the flow of the surface has been observed [Hartek and Reeves, 1964; references in Barrett and Kofsky, these Proceedings]; indeed, interference and saturation of reactive sites are ubiquitous features of surface studies. Presumably these species occupy, or create, sites at which adsorption/excitative desorption occurs. Such an interference effect may be the reason for the "anomalously" rapid increase in intensity of the glow off Atmosphere Explorer at altitudes below 160 km (where atmospheric $[O_2]$ is becoming comparable to $[O]$) reported by Yee and Abreu [1983].

Some Conclusions

A detailed classical trajectory model exists for the more exoergic Rideal-Eley (one participant incident from the gas phase) recombination of O with C adsorbed at three fold sites on the Pt (111) crystal face [Tully, 1980]. The theory predicts that of the ~6 eV exothermicity, statistically 2 eV appears in vibrational, 1 eV in rotational, and 2 eV in translational energy of the CO desorbate, with forward peaking; this result is largely independent of the applied gas-surface interaction potential (which was derived empirically). Experimentally no such high translational energies have been observed for any species/substrate combination; on the other hand even though most of the laboratory results have been interpreted as due to L-H rather than R-E reactions, a similarly large fraction of the available energy in internal excitation is commonly reported (as Table 1 shows). As the interaction potentials and binding energies of upper-atmospheric aeronomic species on the poorly-characterized and in many cases locally inhomogeneous and highly textured surfaces of exposed spacecraft materials are much less well understood, as

is the formation of complexes on them, similar ab initio calculations of the channeling of energy into radiative states of desorbate molecules are unlikely to provide quantitative predictions of glow brightnesses.

Existing information about quantum state-specific surface recombinations, in sum, indicates that when newly-formed molecules are desorbed from transition metals (and some glasses) a high probability exists that their internal energy is comparable to the reaction exothermicity, even when both participants were previously adsorbed on the surface; and that the degree of this excitation, and the surface reaction rate, often depends on the concentration of (oxidizing) surface contaminants, which themselves may be introduced from the incident beam. The database represented by Table 1, comparable NO-NO₂ surface reactions [Barrett and Kofsky, these Proceedings], non-associative desorption and scattering of various species (including in particular NO [Asscher et al., 1985]) from clean model surfaces, and related surface processes are far below the critical mass required for development of credible predictive theory (as is in general the case for catalysis [Somorjai, 1981]). Nonetheless some empirical extrapolation might be made to the largely insulating, rougher-surfaced materials exposed and as putative contaminants on low-Earth-orbiting spacecraft by applying the concepts developed to order the laboratory data (for example formation of complexes at desorption sites). Some further application of these ideas is in the accompanying paper on NO₂ and NO recombination [Barrett and Kofsky, these Proceedings]. Additionally, measurements analogous to those performed in the laboratory of the sensitivity of off-surface emission intensity to substrate temperature--which assesses the binding of reaction participants to the surface, and thus may identify precursor species--and angular distribution of the desorbate flux would complement those already proposed in understanding and scaling spacecraft glow excitation processes.

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TABLE 1. SURFACE RECOMBINATION WITH DESORPTION IN EXCITED STATES

Species [Ref.]	Surface	Conditions*	Excitation state	Comments
N ₂ [1] [2] [3]	Poly Fe Poly Co, Ni Co, Ni, Ag Cu	N permeates, 1150K N in flow tube N and O flow N only, low T _s	X ₂ high v W ³ Δ _u , v≈11 A?(B detected) C (!) 1-2 mm out	T _v depends on S coverage Nitrides necessary Probably W state, see [2] Requires > dissociation energy
CO ₂ [4] [5] [6]	Pt/O Glass Poly Pt	CO flow, 300-600K CO and O flow CO flow, O ₂ gas, 300-1100K	2.6 eV of ν ₃ 3B ₂ (¹ B ₂) T _k ≈3-4T _s	Nonstatistical (first example), O pretreatment needed Visible "continuum" measured T _k decreases off normal, non- statistical, L-H process
CO [7]	Pt/C	O flow, 1400K	High v	Statistical but hot; L-H process
D ₂ O [8]	Pt 111	D ₂ and O ₂ flow, 440-913K	T _k ≈0.5T _s at 90°	Nonstatistical velocity, cos ¹ θ
H ₂ [9] (HD, D ₂) D ₂ [10]	Poly Ni/1/2 S Ni 111/(S)	H permeates, 940-1143K H permeates, 1143K	T _k =1.7T _s at 0° ≈T _s at 90° T _k ≈1.7T _s at 0° ≈0.65T _s at 90°	Nonstatistical velocity, with strong forward peaking Ditto: cos ⁴ θ, distributions independent of S coverage
O ₂ [11] [12] [13]	Ni, Co, Glass Poly Ni Poly Ni	O flow O flow O flow	A, 0.1/recomb A (v=0 & 1), b A, a, b	Glass requires conditioning No OI lines Just as expected from O ³ P
OH [12] ([14])	Ni Poly Pt	O flow H ₂ +O ₂ , H ₂ +NO ₂ , H ₂ O flow, 1130K	A T _v = T _r = T _s	Could be gas-phase artefact All in equilibrium)

NO, NO₂ - Refer to the accompanying reports by Barrett and Kofsky [these Proceedings].

*T_s ≡ surface temperature ≈293K unless stated otherwise; T_k, T_v≡ kinetic, vibrational temperature.